



TITLE:

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(Commemoration Issue Dedicated to
Professor Yoshimasa Takezaki on the
Occasion of his Retirement)

AUTHOR(S):

Mori, Sadayuki

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Primary Processes in the Reaction of Oxygen Atoms with Acrolein

Sadayuki MORI

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Reaction of $O(^3P)$ atoms produced by the mercury photosensitized decomposition of N_2O with acrolein in the vapor phase has been studied at room temperature. The principal reaction products are the polymers of poly-ester type, carbon monoxide, acetaldehyde, water, and glycidaldehyde. The precursor of the polymers is an active intermediate similar to that produced in the photolysis of β -propiolactone. It is deduced that attack of atomic oxygen to the $C=C$ double bond of acrolein is more important ($\sim 90\%$ of all the primary processes) and the hydrogen abstraction from the CHO group is less contributed ($\sim 10\%$).

KEY WORDS: Reaction Mechanism/ Acrolein/ Addition/
Hydrogen Abstraction/

INTRODUCTION

Since it was found that aldehydes were concerned closely with the occurrence of photochemical smog, many studies for the reactions of ground state oxygen (3P) atoms with aldehydes have been carried out. However, many data reported are almost those on saturated aldehydes, and there are few data available for unsaturated aldehydes. Primary step for the reactions of $O(^3P)$ with saturated aldehydes has been assumed to be the abstraction of hydrogen from the aldehydic group. The reaction rates for aldehydes are generally large compared with those for alkanes, alcohols, and ethers, and are comparable to the rates of the addition reaction to olefins. For example, the room temperature rate constants for acetaldehyde and ethylene are $2.9 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ ¹⁾ and $4 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$,²⁾ respectively. On the basis of this fact, it is interesting to investigate whether attacking modes of atomic oxygen to unsaturated aldehyde such as acrolein involve either the abstraction or the addition, or both of them.

Only two data have been reported for the reaction of oxygen atoms with acrolein. Cadle, Lin, and Hausman, Jr.³⁾ have studied the reaction using a discharge-flow method and found the rate constant of $1.6 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ (at room temperature) similar to that of acetaldehyde. Further, they have postulated the abstraction reaction as the primary process on the basis of the fact that the obtained rate constant was very close to that of acetaldehyde.

Gaffney, Atkinson, and Pitts, Jr.⁴⁾ have obtained the rate constant of $2.32 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ from the relative rate in the competitive reaction of acrolein and cyclopentene, but they have given no information on the reaction mechanism.

* 森 貞之: Laboratory of High Pressure Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

In the present work, for the purpose of clarifying the feature of oxygen attack which involves the hydrogen abstraction from the CHO group or the addition to the C=C double bond, or both, a mechanistic investigation for the reaction of oxygen atoms with acrolein has been carried out.

EXPERIMENTAL

The experimental studies were carried out using a usual static system. Ground state (3P) oxygen atoms were generated by the mercury photosensitized decomposition of N_2O . The apparatus used consists of a cylindrical Vycol glass reactor of 117 cm³ volume connected with a mercury saturator, a reactant inlet system, and a product collection system (a cold trap and Toepler pump).

After irradiation of the resonance radiation (253.7 nm) by a low pressure mercury lamp, the produced gas mixture is collected by means of Toepler pump separately. The first fraction is the permanent gas product passed through the cold trap at -196°C , the second is the product gas vaporized at -115°C (ethanol-liquid N_2 slush), and the third is the remainings. These products were analysed separately by gas chromatography. The columns were activated charcoal or Molecular Sieves 5A for the permanent gases, and Porapak Q-S, Porapak N, acetyl tri-butyl citrate or di-iso-decyl phthalate for the others. A gas chromatograph-mass spectrometer was also used for the identification of the products.

N_2O (Takachiho Co., 99.9%) was evacuated at liquid N_2 temperature, and purified by a bulb-to-bulb distillation. Acrolein (Nakarai Chemicals Co.) was purified by a preparative gas chromatography, and kept at a low pressure in a gas reservoir.

RESULTS AND DISCUSSION

1) Mercury photosensitized decomposition of acrolein

Prior to the study on the reaction of oxygen atoms with acrolein, the mercury photosensitized decomposition of acrolein has been examined.

Major products were carbon monoxide and ethylene. Small amounts of acetylene, hydrogen, 1, 3-butadiene, and propionaldehyde were formed. Methane, ethane, acetaldehyde, and propylene were also detected in a trace amount. The ratio of each prod-

Table I. Hg photosensitized decomposition of acrolein.

$p_{\text{Acr}}^{\text{a)}}$ (Torr)	p_{Ar}	$\frac{[\text{Acr}]}{[\text{Acr}]_0}$	Products/Acr consumed								
			H_2	CO	CH_4	C_2H_4	C_2H_2	C_2H_6	1,3- C_4H_6	CH_3CHO	C_2H_5CHO
2.26	61.8	0.907	0.0174	0.342	0.002	0.302	0.035	0.001	0.007	0.001	0.019
0.00485	0.73	0.73		0.925		0.589	0.212	^{b)}			
	(He)										

* Irradiation time is 1.0 min, and temperature is 30°C .

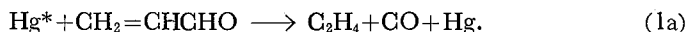
a) Acr refers to acrolein.

b) Ref. (5), Hg photosensitized decomposition of acrolein in a flow system at 55°C .

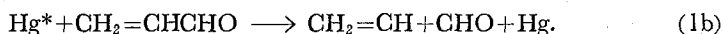
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uct to the consumed acrolein is shown in Table I (an upper line). The material balance of the products found is poor as seen in Table I, and this suggests that a considerable part of the consumed acrolein has been used for the formation of the undetectable products such as polymers. The product distribution found in this experiment can be compared with the other data reported. Harrison and Lossing⁵⁾ have studied the mercury photosensitized decomposition of acrolein using a flow system combined with a mass spectrometer. They have obtained the relatively high yields of products compared with present result because of suppression of the polymerization by using a flow system and a low pressure (shown in a lower line of Table I).

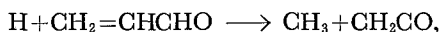
From the result that CO and C₂H₄ were the major products in this work, it can be assumed that the primary process (1a) is principal in the mercury photosensitized decomposition of acrolein,



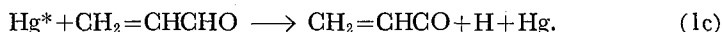
Moreover, the detection of a small amount of 1, 3-butadiene suggests the production of vinyl radicals in the primary process (reaction (1b)) though the contribution may be small,



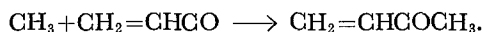
Although the existence of CH₃ radicals is suggested by the observation of CH₄, C₂H₆, and C₃H₈, the formation of these products in the primary process seems to be difficult. For instance, the reactions including hydrogen atoms have to be considered



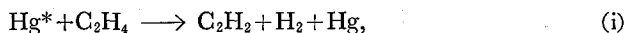
and then, the formation of hydrogen atom (reaction (1c)) may occur as a primary process



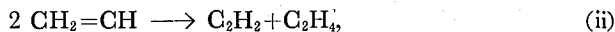
The existence of CH₂=CHCO radicals has been shown by Harrison and Lossing from the result that methyl vinyl ketone was found in the mercury photosensitized decomposition of a mixture of acrolein and dimethyl mercury which could produce CH₃ radicals,



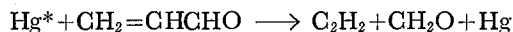
Acetylene was one of the major products in the work of Harrison and Lossing. They have suggested the formation by the subsequent reaction of ethylene



or by the disproportionation of vinyl radicals



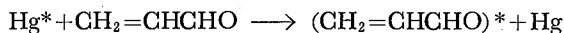
not by a primary process such as



because they have not detected formaldehyde which should be formed concomitantly.

Although a small amount of acetylene ($[C_2H_2] / [C_2H_4] \sim 0.1$) was formed in this experiment, it is not probable that only the molecular decomposition process of ethylene (reaction (i)) is involved for the formation of acetylene by considering a formation of relatively small amounts of H_2 compared with C_2H_2 . So, the reaction (ii) may be also involved.

Consequently, the products formed in this experiment are well explained by these three primary processes (reactions (1a), (1b), and (1c)), but the relative importance in these processes can not be determined because of the low yields in the observed products. For example, it is probable that the polymerization of acrolein may be initiated by the radicals produced in the reactions (1b) and (1c). Moreover, although the activated acrolein formed primarily



can decompose at a low pressure as applied in the work of Harrison and Lossing, it may polymerize at a relatively high pressure as in the present experiment.

2) Reaction of oxygen atoms with acrolein

The study of the reaction of oxygen atoms with acrolein has been carried out under the condition of a large excess of N_2O in order to reduce the mercury photosensitization of acrolein.

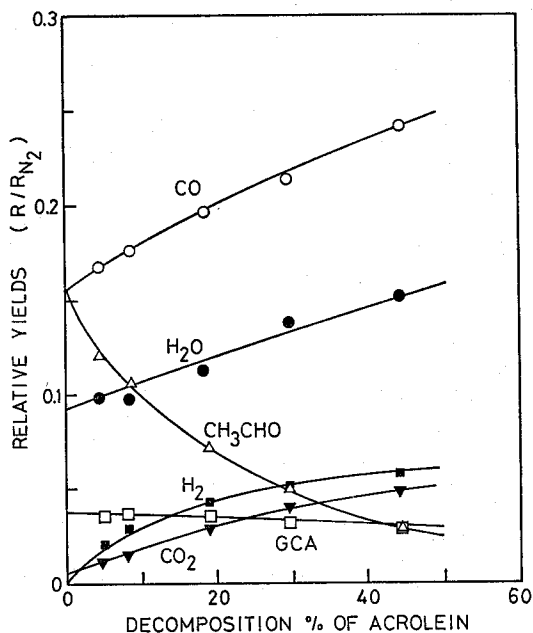


Fig. 1. The variation of the product yields with the decomposition ratio of acrolein. The conditions are shown in Table II.

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may be consumed for the formation of the undetectable compounds such as polymers. Actually, even after a 0.5 min irradiation, a white solid deposit was found in the reactor. Hereupon, the amounts of the consumed acrolein are approximately equal to that of the produced N_2 , and yet the ratio of $\Delta[Acr]/[N_2]$ is independent of the decomposition ratio or the initial concentration of acrolein. Moreover, the co-existence of CH_3 radical in the acetone added experiment (Run 6) was not largely affected the product distribution and could not suppress the polymerization process, though the existence of $CH_2=CHCO$ and $CH_2=CH$ radicals turned out to be evident by a slight increase of the amounts of methyl vinyl ketone and propylene. It suggests that the polymerization of acrolein alone

Major products were CO , CH_3CHO , H_2O , H_2 , CO_2 , and glycidaldehyde. Small amounts of CH_4 , methyl vinyl ketone, C_2H_4 , C_2H_6 , and trace amounts of C_2H_2 and C_3H_6 were also found. These are given in Table II. The relative yields of major products are shown in Fig. 1. As seen in Table II, the total amounts of the observed products are small compared with that of the produced N_2 . The large part of reacted acrolein

Table II. Product distribution in the reaction of $O(^3P) + CH_2=CHCHO$.

Run No.	p_{Acr} (Torr)	p_{N_2O}	$[N_2] \times 10^3$ (mole/cm ³)	$\frac{\Delta[Acr]^a)}{[N_2]}$	$\frac{[Acr]}{[Acr]_0}$	Products/ $Acr_{consumed}$					
						H_2	CO	CH_4	C_2H_4	C_2H_6	CO_2
1	4.31	403.1	1.08	0.992	0.950	0.020	0.168	0.0053	0.0035	0.0008	0.0112
2	5.96	400.7	2.17	1.06	0.928	0.028	0.176	0.0063	0.0050	0.0008	0.0136
3	2.13	403.6	1.81	1.12	0.822	0.043	0.197	0.0078	0.0080	0.0013	0.0280
4	3.91	402.9	5.90	1.00	0.712	0.051	0.212	0.0078	0.0093	0.0014	0.0392
5	2.37	405.8	5.58	1.01	0.544	0.056	0.240	0.0088	0.0086	0.0016	0.0468
6 ^{b)}	2.22	400.0	4.80	1.01	0.596	0.052	0.215	0.0278	0.0074	0.0167	0.0262

Table II. Product distribution in the reaction of $O(^3P) + CH_2=CHCHO$. (Continued)

Run No.	Products/ $Acr_{consumed}$				
	CH_3CHO	MVK ^{c)}	GCA ^{d)}	H_2O	C_3H_6
1	0.119	0.0057	0.0347	0.099	0.0014
2	0.106	0.0056	0.0376	0.098	0.0012
3	0.0705	0.0064	0.0349	0.111	0.0016
4	0.0484	0.0055	0.0320	0.145	0.0019
5	0.0276	0.0032	0.0268	0.150	0.0010
6 ^{b)}	0.0473	0.0160	0.0208	- ^{e)}	0.0050

a) $\Delta[Acr]$ refers to the decrease in the concentration of acrolein resulted from the reaction.

b) In Run 6, 33.0 Torr of acetone was added.

c, d) MVK and GCA refer to methy vinyl ketone ($CH_2=CHCOCH_3$) and glycidaldehyde ($H_2C-CHCHO$), respectively.

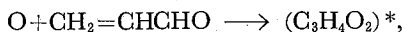


e) Water was not analysed in Run 6.

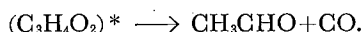
* Less amounts of acetylene ($[C_2H_2]/[C_2H_4] < 0.1$) and propionaldehyde ($[C_2H_5CHO]/[Acr]_{consumed} \sim 0.001$) were also detected in all runs, but are not listed in Table II.

does not occur by the initiators such as $\text{CH}_2=\text{CH}$ radical, because such radicals probably give large amounts of the stable molecules by reacting rapidly with CH_3 radicals.

Moreover, it is seen in Fig. 1 that the amounts of acetaldehyde and carbon monoxide produced are equal at early stage of the reaction, and that as the decomposition ratio of acrolein increases, the initially formed acetaldehyde is consumed by the subsequent reaction, while carbon monoxide and carbon dioxide increase. Therefore, it is inferred that both acetaldehyde and carbon monoxide should be formed in a primary process; that is, an active adduct is formed primarily

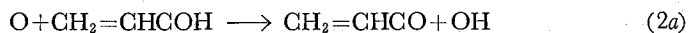


then it decompose to acetaldehyde and carbon monoxide

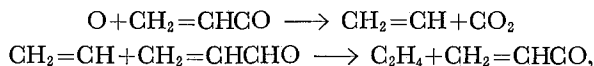


a) *Hydrogen abstraction reaction*

The hydrogen abstraction by oxygen atoms from the CHO group of acrolein (reaction (2a))



has been assumed by Cadle, Lin, and Hausman, Jr.³⁾ from the detection of large amount of ethylene as the reaction product. They have studied the $\text{O}(^3\text{P})$ -acrolein reaction using a discharge-flow method and determined the rate constant for the reaction. They have also estimated roughly the yields of ethylene, acetylene, carbon monoxide, and carbon dioxide to be of the same order, from their infrared absorption. They have suggested that the formation of ethylene may result from a mechanism analogous to that proposed for the $\text{O}(^3\text{P})$ -acetaldehyde reaction,⁶⁾ i. e. the reaction (2a) is followed by



and they have also speculated the formation of acetylene by the addition of atomic oxygen to the $\text{C}=\text{C}$ double bond of acrolein.

In this work, as the yield of ethylene was very small and that of carbon dioxide was also small compared with that of carbon monoxide, the mechanism proposed by Cadle *et al.* can not be applied to the present reaction system. However, as seen in Fig. 1, the yield of water approaches to a limiting value not to be zero when the decomposition ratio of acrolein approaches to zero. This suggests that OH radical can be produced in the primary process of the atomic oxygen-acrolein reaction. The reaction (2a) may also be supported by the existence of $\text{CH}_2=\text{CHCO}$ radical which was verified with the fact that a small amount of methyl vinyl ketone was detected and its yield increased in the acetone-added system. OH radicals produced in the reaction (2a) abstract a hydrogen atom from acrolein or other products, and result in the formation of water (in the case of crotonaldehyde, OH radicals are suggested to abstract a hydrogen from the CHO group of crotonaldehyde⁷⁾).

The relative importance of the reaction (2a) can be estimated to be about 10% of

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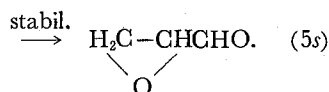
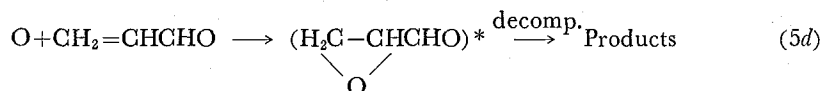
all the primary processes from the yield of water when the decomposition ratio of acrolein approaches to zero.

b) Addition reaction

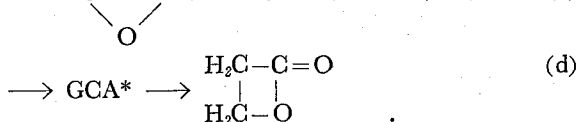
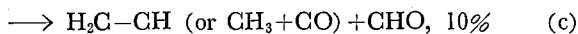
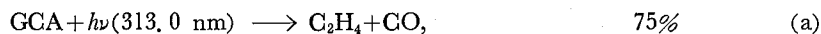
Glycidaldehyde ($\text{H}_2\text{C}-\text{CHCHO}$, referred to as GCA in the following) was found as



the reaction product in this work. As the yield of GCA does not vary even if the decomposition ratio of acrolein increases, its formation in a primary process is suggested. It is evident that GCA is formed by the addition of atomic oxygen to the $\text{C}=\text{C}$ double bond of acrolein followed by the collisional stabilization, *i. e.*



Concerning about the decomposition process (5d), acetaldehyde and carbon monoxide, which were the major products observed in this work, may be formed through this active GCA intermediate. On the other hand, Goodspeed and Blacet⁹⁾ have postulated the primary processes in the photolysis of GCA as



In the present work, the yields of ethylene and carbon dioxide formed at a early stage of the reaction are very small compared with those of acetaldehyde and carbon monoxide. Therefore, it is unlikely that acetaldehyde and carbon monoxide are formed by way of the active GCA intermediate. On the other hand, as seen in Fig. 2, the yield of GCA decreases at a lower pressure, and the decrease in the yield of GCA is comparable to the increase in that of ethylene or carbon dioxide (see also Fig. 3). This means that in the present reaction, GCA decompose *via* the processes analogous to those in the photolysis of GCA.

c) Polymer formation

As described above, a white solid deposit was found in the reactor for all runs. This substance was insoluble in water, acetone or methanol, and could not be removed by heating with conc. H_2SO_4 . But heating with conc. aq. NaOH solution, it could be easily removed. This suggests strongly that this substance is a ester type polymer. β -Propiolactone, for example, is conceivable for the precursor of this ester type polymer. It has been reported that the polymers of β -propiolactone are poly-ester acid (II) which varies from colorless viscous oils to white solids depending on the degree of polymerization,⁹⁾

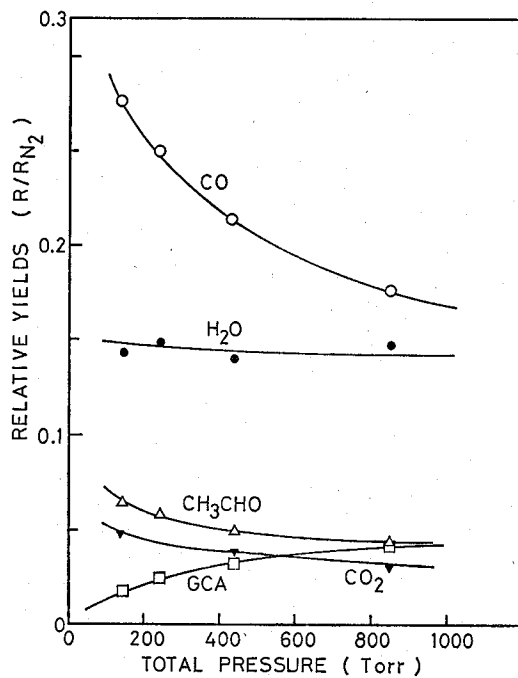


Fig. 2. Pressure effects on the product yields (major products). Conditions are; $p_{\text{Acr}}=1.4$ Torr, irradiation time is 60 sec, $A[\text{Acr}]/[\text{Acr}]_0=0.30$, $T=27^\circ\text{C}$.

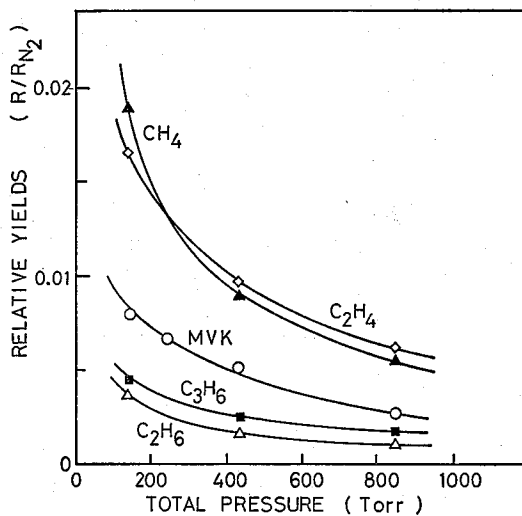
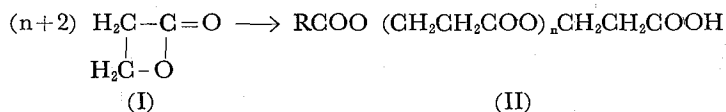
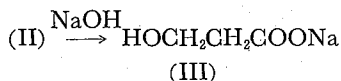


Fig. 3. Pressure effects on the product yields (minor products). Conditions are the same as in Fig. 2.

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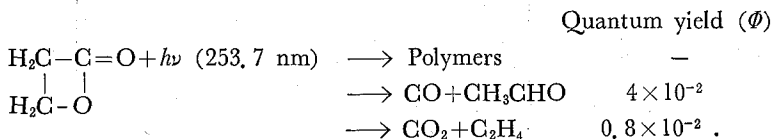


and in boiling aqueous caustic, they are saponified to salts of hydracrylic acid (III),

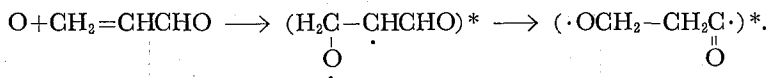


These characteristics are similar to those of the deposit formed in this work. Therefore, it can be inferred that the unit of the polymers formed in this work may be $-\text{CH}_2\text{CH}_2\text{COO}-$ or $-\text{OCH}_2\text{CH}_2\text{CO}-$.

Linnell and Noyes, Jr.¹⁰ have found large amounts of polymers and small amounts of gaseous products such as CO , CO_2 , C_2H_4 , and CH_3CHO in the photolysis of β -propiolactone in a liquid phase, and they have suggested the following processes,



By analogies in the characteristics of the polymers as described above and in the product distributions in this work and the photolysis of β -propiolactone, it can be deduced that the reaction of oxygen atoms with acrolein proceeds by way of an active intermediate similar to that involved in the photolysis of β -propiolactone; that is, the addition of atomic oxygen to the $\text{C}=\text{C}$ double bond of acrolein followed by the hydrogen atom migration,



This intermediate may yield the polymers or decompose to $\text{CO} + \text{CH}_3\text{CHO}$ mainly or to $\text{CO}_2 + \text{C}_2\text{H}_4$ with a small contribution.

The formation of β -propiolactone was not observed, and this means that the active

Table III. C, H and O balances in the reaction products.

Run No.	$\Delta[\text{Acr}]/[\text{Acr}]_0$ (%)	Observed products				Undetectable products			
		α^a	C	H	O	$(1-\alpha)$	C	H	O ^b
1	5.0	0.171	3.00	5.50	2.68	0.829	3.00	3.69	1.90
2	7.2	0.160	3.00	5.90	2.88	0.840	3.00	3.62	1.80
3	17.8	0.171	3.00	4.99	2.89	0.829	3.00	3.80	1.73
4	28.8	0.172	3.00	4.81	2.94	0.828	3.00	3.83	1.81
5	44.6	0.163	3.00	4.77	3.44	0.837	3.00	3.85	1.67

a) α shows a ratio of the total amounts of carbon atoms observed to those consumed.

b) O balance in the undetectable products is estimated from $\Delta[\text{Acr}]/[\text{N}_2]$ in Table II and O_{observed} in this Table.

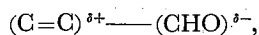
intermediate does not lead to β -propiolactone by collisional deactivation.

The C, H and O balances in the undetectable products involving the polymers were calculated from the amounts of observed products, those of consumed oxygen atoms, and those of consumed acrolein. These are given in Table III. The ratios of C, H, and O in the undetectable products are approximately $C_3H_4O_2$ as seen in Table III and this means that the polymers (or undetected substances) are consisted of the adduct of oxygen/acrolein=1 and are not the polymers of acrolein alone $(C_2H_4O)_n$. A slightly small value in the balances of H and O can be attributed to the contribution of radicals such as $CH_2=CH$, $CH_2=CHCO$, or CH_3 to the formation of the polymers. Moreover, the ratio of the observed carbon atoms to the undetected amounts of carbon atoms, $\alpha/(1-\alpha)$, are not varied even when acrolein decomposed largely (up to 45%), and this suggests that the polymerization does not proceed *via* the subsequent reactions of oxygen atoms with the initially formed products.

d) *Mode of the oxygen atom attack on acrolein*

The hydrogen abstraction reaction, which has been assumed by Cadle, Lin, and Hausman, Jr. for the reaction of oxygen atoms with acrolein, is found to have a less contribution (about 10%) to the total primary processes as shown above.

It has been suggested that oxygen atoms are electrophilic in nature in the addition to olefins.¹¹⁾ In the case of acrolein, the carbonyl group attracts electrons from the C=C bond, and a partially polarized structure is well known,



and the molecular orbital calculation for acrolein (*ab initio* SCF with STO-3G) also gives the total π electron densities as¹²⁾

$$\begin{array}{cc} (C=C) & (CHO) \\ q^{\pi} & 1.963 \quad 2.037 \end{array}$$

This suggests a slightly decrease of the double bond nature at the C=C bond. And the rate for the attack of atomic oxygen on the C=C double bond of acrolein is expected to decrease in comparison with that of ethylene. Actually, the lower value of the rate constant for the $O(^3P)$ -acrolein reaction have been reported ($1.6 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ or $2.3 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$)^{3,4)} compared with that for the $O(^3P)$ -ethylene reaction ($4 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$).²⁾

Moreover, this molecular orbital calculation gives higher electron densities at both end atoms in the frontier orbitals such as

$$\begin{array}{ccccc} & C & \text{---} & C & \text{---} & C & \text{---} & O \\ f_r^{(R)} & 0.688 & & 0.662 & & 0.355 & & 0.657 \\ f_r^{(E)} & 0.586 & & 0.217 & & 0.202 & & 0.577 \end{array}$$

where $f_r^{(R)}$ is the frontier electron density on r th atom for radical reactions and $f_r^{(E)}$ is that for electrophilic reactions.

The reactivity is expected to be large at both end atoms (the end carbon of the C=C and oxygen of the CHO) for both radical or electrophilic reactions. However, the attack of atomic oxygen on oxygen of the CHO group is improbable because of the

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repulsion between the lone pair electrons of each other, and thus oxygen atoms attack inevitably the C=C double bond.

In the present work, the reaction products can be explained by assuming that the major course of the reaction is the addition of atomic oxygen to the C=C double bond and the minor is the abstraction from the CHO group.

e) Pressure effects and the mechanism

Almost all of the observed products (besides water and GCA) are increased by decreasing the total pressure as seen in Fig. 2 and 3. This suggests that these products are produced by the decomposition of active intermediate as described above.

The same calculation as in Table III has been carried out for the different conditions of total pressure (Table IV). As seen in Table IV, α (the ratio of the amount of observed carbon atoms to that of consumed carbon atoms) seems to be slightly large at

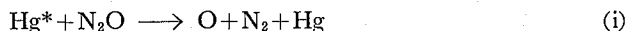
Table IV. Pressure effect on the C, H and O balances.

Total pressure (Torr)	α^a	Undetectable products			
		(1- α)	C	H	O
135	0.198	0.802	3.00	3.82	1.72
435	0.172	0.828	3.00	3.83	1.81
833	0.157	0.843	3.00	3.80	1.76

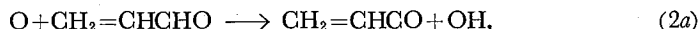
a) α is the same as in Table III.

a lower pressure, and this means that the species which should lead to the polymers or the undetectable products at higher pressure decomposes at lower pressure. However, the C, H and O balances in the undetectable products are independent with the total pressure, and therefore, a similar reaction is suggested for the formation of the polymers or undetectable compounds in this pressure range.

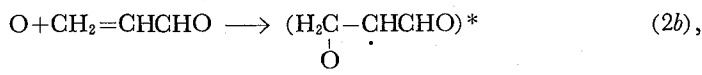
On the basis of the processes for the product formation discussed above, the following mechanism can be assumed; *i. e.*



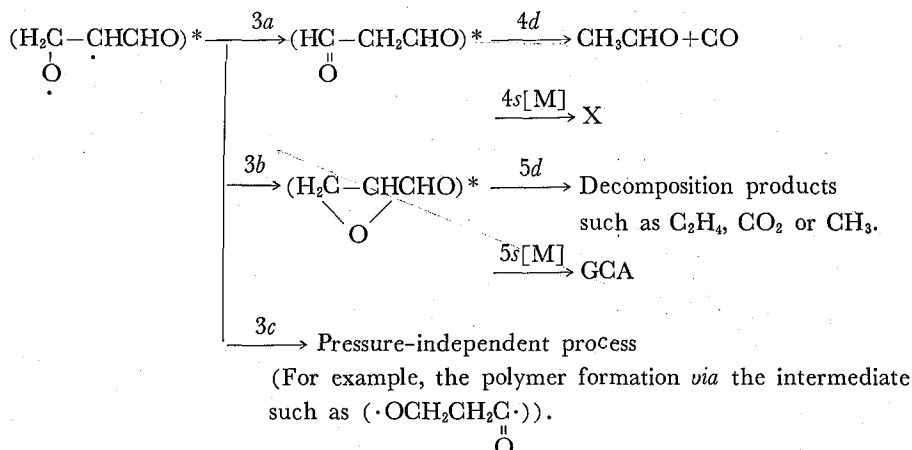
when atomic oxygen attacks the carbonyl group of acrolein, the hydrogen abstraction occurs



while, in case of its attack on the C=C bond, the addition to the end carbon atom occurs in the same way as the case of 1,3-butadiene,¹³⁾



and this active bi-radical may react *via* the following processes



Here, the intermediate in the process (3a) is postulated as the formation of CO and CH₃CHO depends on the total pressure, though there is no direct evidence for it. And X refers to the undetectable compound which is conjectured to be produced by the collisional deactivation.

Using this mechanism, the formation of GCA can be expressed as

$$\frac{R_{\text{GCA}}}{R_{\text{N}_2}} = \frac{k_{2b}k_{3b}}{k_2k_3} \left(\frac{1}{1 + k_{5d}/k_{5s}[\text{M}]} \right) \quad (\text{I})$$

where $k_2 = k_{2a} + k_{2b}$, and $k_3 = k_{3a} + k_{3b} + k_{3c}$.

The plot of $R_{\text{N}_2}/R_{\text{GCA}}$ against reciprocal total pressure is shown in Fig. 4 (Data are the same as in Fig. 2). From the intercept, $k_{3b}/k_3 \simeq 0.08$ is obtained assuming $k_{2b}/k_2 \simeq 0.9$ (as $k_{2a}/k_2 \simeq 0.1$ has been shown above). From the slope, $k_{5d}/k_{5s} = 1.7 \times 10^{-5}$ mole cm⁻³ is obtained.

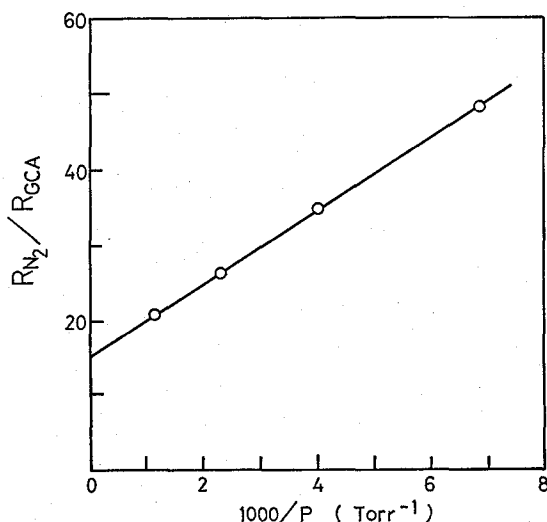


Fig. 4. Plot of $R_{\text{N}_2}/R_{\text{GCA}}$ against reciprocal total pressure.

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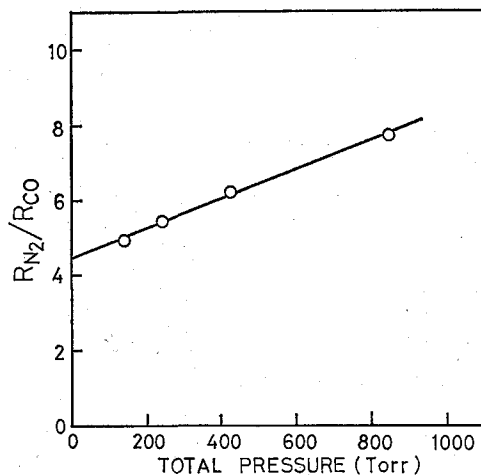


Fig. 5. Pressure effect on the CO yield.

Table V. Life times of "hot" addition products

Reacting molecule	"Hot" product	Life time (sec)
C_2H_4	CH_3CHO	3×10^{-10}
$CH_2=CHCHO^a$	$H_2C-CHCHO$	1×10^{-9}
$H_2C=CHCH=CH_2$	$H_2C=CHCH_2CHO$	1.4×10^{-9}
$H_2C=CHCH=CH_2$	$H_2C-CHCH=CH_2$	2.7×10^{-9}
$CH_2=CHCH_3$	$H_2C-CHCH_3$	5.8×10^{-9}

a) This work.

Data except for of acrolein are from Ref. (14).

When it is assumed that deactivation occurs at approximately every collision, the life time of the "hot" GCA is calculated to be $1/k_{sd} \approx 1 \times 10^{-9}$ sec. As seen in Table V, this value is similar to that of "hot" 1-butenal and is smaller than that of butadiene monoxide or propylene oxide, suggesting the "hot" GCA to be more unstable than the last two.

Meanwhile, concerning about the CO formation, steady-state treatment in the above mechanism leads to the following expression,

$$\frac{R_{N_2}}{R_{CO}} = \frac{k_2 k_3}{k_{2b} k_{3b}} \left(1 + \frac{k_{4s}}{k_{4d}} [M] \right). \quad (II)$$

The plot of R_{N_2}/R_{CO} against total pressure is shown in Fig. 5. From this, $k_{3a}/k_3 \approx 0.25$ is obtained, where for the yields of CO the limiting value at the decomposition ratio of zero were used (the variation of the CO yield *vs.* the decomposition ratio of acrolein has been examined for only the experiment at 435 Torr, but it is assumed that the for-

mation of carbon monoxide by the subsequent processes is not so much affected by a total pressure).

From the estimated values of k_{3a}/k_3 and k_{3b}/k_3 , $k_{3a}/k_3 \simeq 0.67$ is obtained for the pressure-independent process; *i. e.* a good part of the addition intermediates participate in the formation of the undetectable products such as polymers.

Consequently it is suggested that the greater part of the primary processes in the atomic oxygen-acrolein reaction occurs at the C=C double bond (90%), while the hydrogen abstraction from the CHO group is less contributed (10%), and the active intermediates formed by the oxygen atom addition to the C=C double bond result mainly in the polymers (60% of total primary processes), and small fractions of them are involved in the processes for the formation of CO+CH₃CHO (23%) and glycidaldehyde (7%).

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